



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



⑪ Publication number:

**0 159 117 B1**

⑫

## EUROPEAN PATENT SPECIFICATION

⑯ Date of publication of patent specification: **27.01.93** ⑯ Int. Cl. 5: **C07D 231/12, C08G 18/80, C08G 18/10, C09D 5/44**

⑯ Application number: **85301298.7**

⑯ Date of filing: **26.02.85**

The file contains technical information submitted after the application was filed and not included in this specification

⑯ **Blocked Isocyanates.**

⑯ Priority: **29.02.84 GB 8405320**

⑯ Date of publication of application:  
**23.10.85 Bulletin 85/43**

⑯ Publication of the grant of the patent:  
**27.01.93 Bulletin 93/04**

⑯ Designated Contracting States:  
**AT BE CH DE FR GB IT LI LU NL SE**

⑯ References cited:  
**GB-A- 2 153 346  
SU-A- 414 259  
US-A- 3 721 645  
US-A- 4 008 247  
US-A- 4 335 228**

⑯ Proprietor: **THE BAXENDEN CHEMICAL COMPANY LIMITED  
Paragon Works  
Baxenden, Near Accrington Lancashire BB5 2SL(GB)**

⑯ Inventor: **Hughes, Anthony  
Collinge Fold Farm  
Rossendale, Lancashire(GB)  
Inventor: Topham, Arthur  
34 Dingle Road, Alkrington  
Middleton, Manchester(GB)**

⑯ Representative: **Goldin, Douglas Michael et al  
J.A. KEMP & CO. 14, South Square Gray's Inn  
London WC1R 5EU(GB)**

**EP 0 159 117 B1**

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid (Art. 99(1) European patent convention).

## Des ription

The present invention relates to coating and other compositions e.g. paints and elastomers, containing certain blocked isocyanates and methods of electrodeposition of the coating compositions.

5 Blocked polyisocyanates are commonly used in paints which also contain active hydrogen containing compounds e.g. amines and alcohols. Certain of these paints can be electrophoretically or conventionally e.g. spray deposited onto the article to be coated and then subsequently hardened by heating, often referred to as stoving. During stoving the blocked polyisocyanates dissociate so that the isocyanate groups become available to react with the active hydrogen containing compounds leading to crosslinking and 10 hardening of the paint.

Blocked polyisocyanates reacting with any active hydrogen containing compound for the purposes of curing by chain extension or crosslinking are also used in crosslinking acrylic resins for automotive priming and finishing, formulating one-pack elastomers and surface coatings which contain the blocked isocyanate and as a chain extender in a single storage stable package which, when cast, can be cured by application 15 of temperatures above the unblocking temperature.

Blocked polyisocyanates are polyisocyanates in which each isocyanate group has reacted with a protecting or blocking agent to form a derivative which will dissociate on heating to remove the protecting or blocking agent and release the reactive isocyanate group.

20 Compounds already known and used as blocking agents for polyisocyanates include aliphatic, cycloaliphatic or aralkyl monohydric alcohols, hydroxylamines and ketoximas.

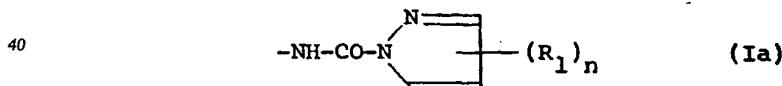
USSR Certificate of Invention No 414259 describes production of certain aromatic polyisocyanates blocked with 3-methylpyrazole.

25 Currently used blocked polyisocyanates dissociate at temperatures of around 160°C. If a blocked polyisocyanate could be used which dissociated at a lower temperature but was still stable at ambient temperatures, then heat sensitive materials could be utilised and energy savings could be made. The blocked polyisocyanates of the present invention dissociate at a significantly lower temperature than those currently used and are easily made. The presence of a catalyst is preferred in order to increase the rate of reaction between the liberated polyisocyanate and the active hydrogen containing compound, especially if the active hydrogen group is -OH. The catalyst can be any catalyst known in the art, e.g. dibutyl tin 30 dilaurate or triethylene diamine.

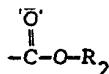
The present invention comprises a compound of the formula:

R-Y<sub>m</sub> (I)

35 where R is an m valent cycloaliphatic, heterocyclic or aromatic residue and each Y, which may be the same or different, is



45 where R<sub>1</sub> is, or, when n is more than 1, each R<sub>1</sub>, which may be the same or different, is an alkyl, alkenyl, aralkyl, N-substituted carbamyl, phenyl, NO<sub>2</sub>, halogen or

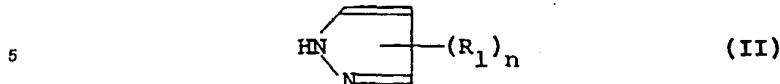


50 group where R<sub>2</sub> is a C<sub>1</sub>-C<sub>4</sub> alkyl group, n is 0, 1, 2 or 3 and m is an integer > 1, preferably 2-6, provided that, when R is an aromatic residue, the groups Y are not directly attached to the aromatic nucleus.

The invention also extends to coating compositions based on such blocked polyisocyanates but in 55 which R may additionally be an aliphatic residue.

When R<sub>1</sub> represents an alkyl or alkenyl group it preferably contains up to 4 carbon atoms. When it is an aralkyl group, it is preferred that the aryl portion is phenyl and that the alkyl portion contains 1 to 4 carbon atoms. When R<sub>1</sub> is a halogen, it is preferably chlorine or bromine.

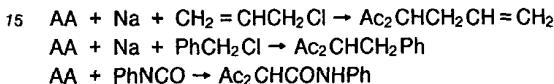
The blocking agents used in the present invention are pyrazoles of the formula:



where  $R_1$  and  $n$  are as defined above. Examples of the pyrazoles described include 3,5-dimethylpyrazole, 10 3-methylpyrazole, 4-nitro-3,5-dimethylpyrazole and 4-bromo-3,5-dimethylpyrazole.

The preferred blocking agent is 3,5-dimethylpyrazole.

Some of these pyrazoles can be made by converting acetylacetone (AA) into a derivative which will react with hydrazine to give the desired pyrazole e.g.



The polyisocyanate which is to be blocked may be any organic polyisocyanate suitable for crosslinking 20 compounds containing active hydrogen e.g. aliphatic including cycloaliphatic, aromatic, heterocyclic, and mixed aliphatic aromatic polyisocyanates containing 2, 3 or more isocyanate groups. The group R will normally be a hydrocarbon group but substitution e.g. by alkoxy groups is possible.

The isocyanate compound may be, for example, ethylene diisocyanate, propylene diisocyanate, 25 tetramethylene diisocyanate, hexamethylene diisocyanate, decamethylene diisocyanate, dodecamethylene diisocyanate, 2,4,4-trimethylhexamethylene-1,6 diisocyanate,  $\omega,\omega'$ -diisocyanato-1,3-dimethyl benzene,  $\omega,\omega'$ -diisocyanato-1,4-dimethyl cyclohexane,  $\omega,\omega'$ -diisocyanato-1,4-dimethyl benzene,  $\omega,\omega'$ -diisocyanato-1,3-dimethylcyclohexane, 1-methyl-2,4-diisocyanato cyclohexane, 4,4'-methylene-bis (cyclohexyl isocyanate), 30 3-isocyanato-methyl-3,5,5-trimethyl cyclohexyl isocyanate, dimer acid-diisocyanate,  $\omega,\omega'$ -diisocyanato-diethyl benzene,  $\omega,\omega'$ -diisocyanatodimethyl toluene,  $\omega,\omega'$ -diisocyanato-diethyl toluene, fumaric acid-bis (2-isocyanato ethyl) ester or triphenyl-methane-triisocyanate, 1,4-bis-(2-isocyanato-prop-2-yl) benzene, 1,3-bis-(2-isocyanato prop-2-yl) benzene, but is preferably free from isocyanate groups directly attached to aromatic nuclei.

Use can also be made of polyisocyanates obtained by reaction of an excess amount of the isocyanate with a) water, b) a lower molecular weight polyol (e.g. m.w.  $\leq 300$ ) or c) a medium molecular weight polyol, 35 e.g. a polyol of greater than 300 and less than 8000 m.w., eg sucrose, or by the reaction of the isocyanate with itself to give an isocyanurate.

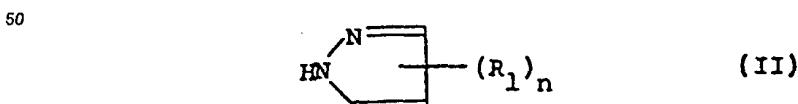
The lower molecular weight polyol comprises, for example, ethyleneglycol, propyleneglycol, 1,3-butylene glycol, neopentyl glycol, 2,2,4-trimethyl-1,3-pentane diol, hexamethylene glycol, cyclohexane dimethanol, hydrogenated bisphenol-A, trimethylol propane, trimethylol ethane, 1,2,6-hexane triol, glycerine, 40 sorbitol or pentaerythritol.

The di- or poly-isocyanate obtained by the above reaction may have a biuret structure, or an allophanate group.

The blocked polyisocyanate of the formula I is formed by admixing the polyisocyanate

45  $R(NCO)_m$  (III)

with a sufficient quantity of a pyrazole of the formula:



55 such that the reaction product contains no free isocyanate groups and is a urea of formula I. This reaction is exothermic and since the reaction product will dissociate if the temperature is raised sufficiently, cooling may be required to keep the temperature of the reaction mixture down, preferably to 80°C or less.

One use of blocked polyisocyanates is in coating compositions, as defined in the claims, especially in electrophoretically deposited paints. The invention also comprises a paint composition comprising a pigment carrier containing active hydrogen groups, a pigment and a compound of the formula I.

These paints are usually composed of a pigment dispersed in an aqueous dispersion of a resin containing active hydrogen which is to be crosslinked by the polyisocyanate. Preferably the paint contains 0.5 to 2 blocked isocyanate groups per active hydrogen containing group. Suitable active hydrogen containing resins include polyamide-polyamine resins, e.g. the product from a dimer fatty acid and an aliphatic polyamine, carboxylic acid group containing acrylic resins, and tertiary amine group containing hydroxyacrylic resins and polymers thereof.

10 The total concentration of the dispersed solids will, of course, depend upon the process for which the paint is to be used. Various standard additives such as surface active agents, catalysts and anti-oxidants may also be incorporated.

15 The invention also comprises coating processes as defined in the claims, particularly a method of electrodepositing onto substrates a paint composition as described above and then heating the deposited paint to cross link the pigment carrier.

The electrophoretic deposition process is well known and involves the use of a cathode and an anode in contact with a bath containing the paint. The surface to be coated is one of the electrodes. On applying a voltage, generally 1 to 3,000 volts, across the electrodes the paint is deposited over the chosen electrode.

20 The coated article is removed from the bath and stoved e.g. baked in an oven, in order to release the isocyanate groups which then react with the active hydrogen in the resin to crosslink and harden the coating. Using coating compositions according to this invention the temperature to which the coated article must be heated is generally 100 to 120 °C, which is significantly lower than the temperatures required in current commercial processes of 160 °C or more.

25 An added advantage of the process of our invention is the ability to block polyisocyanates in the presence of alcoholic solvents, because pyrazoles are much more reactive than alcohols towards polyisocyanates. This also makes it possible to block polyisocyanates at temperatures lower than those used with compounds already known and used as blocking agents for polyisocyanates.

30 The following Examples illustrate the invention. All parts and percentages are by weight unless otherwise specified.

#### Example 1

A mixture of 91.5 parts of trimethylolpropane, 273.2 parts of propylene carbonate and 454.9 parts of isophorone diisocyanate is stirred for 2½ hours at 70 °C and then held at 55 °C for 16 hours. The product thus formed contains 10.37% NCO. 809.3 parts of this product is stirred at 33 °C while 201.0 parts of 3,5-dimethylpyrazole is added, followed by 470.8 parts of the monomethyl ether of propylene glycol (Dowanol PM). The temperature rises to 52 °C and a clear solution is formed. The IR spectrum shows NCO absent. Analysis shows only 0.5% of free dimethylpyrazole to be present.

#### Example 2

A mixture of 861 parts of isophorone diisocyanate, 535.95 parts of propylene carbonate and 2.15 parts of Dabco TMR\* is stirred and gradually heated. When the temperature reaches 55 °C heating is discontinued. The exothermic reaction raises the temperature to 131 °C in 15 minutes. After cooling to 89 °C, 5.8 parts of a 10% solution of Dabco TMR\* in propylene carbonate is added. The temperature rises to 90 °C in 8 minutes. After heating to 132 °C it is allowed to cool. 1397.1 parts of this product, the tri-isocyanato-isocyanurate formed from 3 moles of isophorone di-isocyanate as a 61.4% solids solution in propylene carbonate, having an NCO content of 10.94% is stirred while 366.8 parts of 3,5-dimethylpyrazole is added, cooling as required, to keep the temperature below 80 °C. followed by 463.4 parts of the monomethyl ether of propylene glycol. The mixture is stirred at 50 °C and a clear solution formed which solution is then allowed to cool. The IR Spectrum shows NCO absent.

#### Example 3

55 The preparation referred to in Example 1 above using 3,5-dimethylpyrazole (3,5-DMP) as the blocking agent, was repeated but methyl ethyl ketoxime (MEKO) was used as the blocking agent. The products of

\* (Reg. Trade Mark) which is N-Hydroxyalkyl Quaternary Ammonium Carboxylate.

each of these preparations was then mixed with the stoichiometric quantity of 1,4-butanediol and 1% dibutyltin dilaurate was added and then the mixture was coated onto steel panels. The coatings were allowed to dry at room temperature for 5 days and then stoved in an oven at the specified temperature for 30 minutes. The panels were then tested for pencil hardness as an indication of cure.

5

Temperature in °C	MEKO Blocked	3,5-DMP Blocked
10	100 Fails HB, no cohesive strength	Fails HB, no cohesive strength
	120 Fails HB, no cohesive strength	Passes 5H, cohesive film
	135 Fails HB, no cohesive strength	Passes 7H, cohesive film
	160 Passes 7H, cohesive film	Passes 7H, cohesive film

The above results show an almost 40°C improvement in cure temperature with the 3,5-dimethylpyrazole blocked polyisocyanate.

15

#### Example 4

A paint base is made from the following:-

20

	parts
1. Xylene	7.90
2. Titanium Dioxide RTC60 *(1)	38.27
3. Additive T.I. *(2)	1.60
4. 10% Acronal 700L Solution in Xylene *(3)	0.40
5. Multiflow *(4)	0.13
6. Syncure 867S *(5)	51.70

\*(1) RTC60 - Tioxide U.K. Ltd

\*(2) Additive T.I. - Bayer U.K. Ltd.

\*(3) Acronal 700L - BASF U.K. Ltd

\*(4) Multiflow - Monsanto PLC

\*(5) Syncure 867S - Cray Valley Products Ltd

35

#### METHOD

Charge the Xylene, Additive T.I., 10% Acronal Solution and Multiflow, gradually adding the Titanium Dioxide and half of the Syncure to give sufficient wetting for efficient grinding. Grind under high shear to Hegmann 5, then add the rest of the Syncure.

A mixture of 58.0 parts of the above described paint base, 22.2 parts of the product from Example 1 and 0.4 part of dibutyltin dilaurate was coated on two steel panels and allowed to dry for seven days at ambient temperature. One panel was stoved for 1/2 hour at 120°, and the other for 3/4 hour at 100° C. Tests for pencil hardness showed that both passed 5H.

Similar results (5H pencil hardness) were obtained using equivalent amounts of the products prepared as described in Example 1 but using instead of 3,5-dimethylpyrazole the equivalent amounts of 4-nitro-3,5-dimethylpyrazole, 4-benzyl-3,5-dimethylpyrazole, methyl 5-methylpyrazole-3-carboxylate, 4-bromo-3,5-dimethylpyrazole, pyrazole, 3-methyl-5-phenylpyrazole and 3,5-dimethylpyrazole-4-carboxanilide (prepared by condensation of hydrazine acetate with diacetoacetanilide). A similar result was also obtained using a product prepared as described in Example 1 but using Pentoxone\*(4-methoxy-4-methylpentan-2-one) instead of propylene carbonate. A panel coated with the paint base and stoved for 1 hour at 120° with no crosslinker present failed an HB pencil test.

55

#### Claims

\*Pentoxone - Shell Chemicals PLC

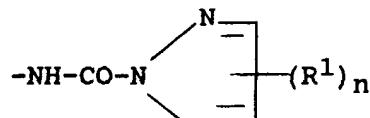
## 1. A blocked polyisocyanate of the formula: (I)

R-Y<sub>m</sub> (I)

5 wherein m is an integer greater than 1;  
 R is an m valent, cycloaliphatic, heterocyclic or aromatic residue;

each Y, which may be the same or different, is

10



15

in which n is 0, 1, 2 or 3;

when n is 1,

R<sup>1</sup> is selected from alkyl, alkenyl, aralkyl, N-substituted carbamyl, phenyl, NO<sub>2</sub>, halogen or -CO-O-R<sup>2</sup> where R<sup>2</sup> is C<sub>1</sub>-C<sub>4</sub> alkyl;

20

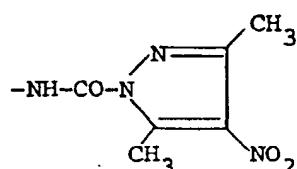
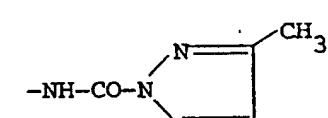
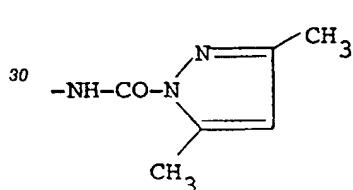
when n is more than 1,

the groups R<sup>1</sup> may be the same or different and each is selected from alkyl, alkenyl, aralkyl, N-substituted carbamyl, phenyl, NO<sub>2</sub>, halogen and -CO-O-R<sup>2</sup> where R<sup>2</sup> is C<sub>1</sub>-C<sub>4</sub> alkyl;

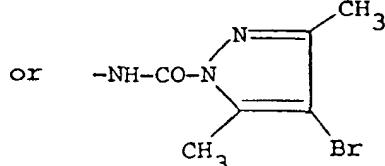
provided that, when R is an aromatic residue, the groups Y are not directly attached to an aromatic nucleus.

25

## 2. A blocked polyisocyanate according to claim 1 wherein at least one Y is



35

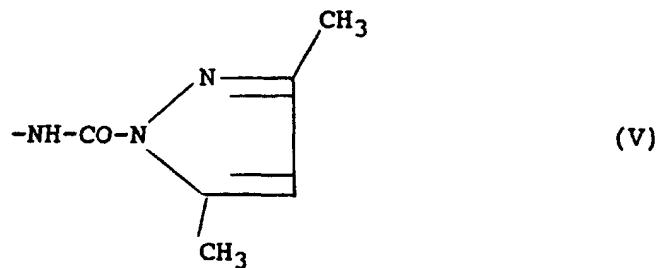


40

45

## 3. A blocked polyisocyanate according to claim 2 wherein at least one Y is

45

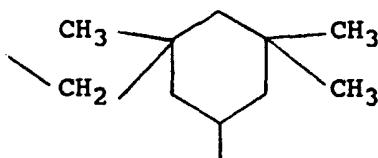


4. A blocked polyisocyanate according to any one of the preceding claims wherein m is from 2 to 6.

5. A blocked polyisocyanate according to any one of the preceding claims wherein R is a hydrocarbon group optionally substituted by an alkoxy group.

5 6. A blocked polyisocyanate according to Claim 1 wherein R is a divalent radical derived from isophorone of formula:

10



15

20 7. A blocked polyisocyanate according to any one of claims 1 to 6 wherein R is the residue of a polyisocyanate reaction product of an isocyanate and water, a lower molecular weight polyol having a molecular weight less than or equal to 300 or a medium molecular weight polyol having a molecular weight greater than 300 and less than 8000.

25 8. A blocked polyisocyanate according to claim 7 wherein R is the residue of a polyisocyanate reaction product of an isocyanate and a lower molecular weight polyol selected from ethylene glycol, propylene glycol, 1,3-butylene glycol, neopentyl glycol, 2,2,4-trimethyl-1,3-pentane diol, hexamethylene glycol, cyclohexane dimethanol, hydrogenated bisphenol-A, trimethylol propane, trimethylol ethane, 1,2,6-hexane triol, glycerine, sorbitol and pentaerythritol.

30 9. A blocked polyisocyanate according to any one of claims 1 to 6 wherein R is the residue of an isocyanurate.

35 10. A blocked polyisocyanate according to any one of the preceding claims which has a biuret structure or an allophanate group.

11. A process for producing a blocked polyisocyanate as claimed in any one of the preceding claims which comprises admixing a polyisocyanate of formula



with a quantity of a pyrazole of formula

45



50

where R, m and n are as defined in claim 1 such that the reaction product contains no free isocyanate groups.

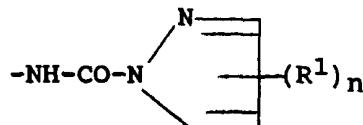
55 12. A coating composition which comprises an active hydrogen-containing compound and a blocked polyisocyanate characterised in that the blocked polyisocyanate is a compound of formula



wherein m is an integer greater than 1;  
 R is an m valent aliphatic, cycloaliphatic, heterocyclic or aromatic residue;

5 each Y, which may be the same or different, is

10



in which n is 0, 1, 2 or 3;

15 when n is 1, R¹ is selected from alkyl, alkenyl, aralkyl, N-substituted carbamyl, phenyl, NO₂, halogen or -CO-O-R² where R² is C₁-C₄ alkyl;  
 when n is more than 1, the groups R¹ may be the same or different and each is selected from alkyl, alkenyl, aralkyl, N-substituted carbamyl, phenyl, NO₂, halogen and -CO-O-R² where R² is C₁-C₄ alkyl;  
 20 provided that, when R is an aromatic residue, the groups Y are not directly attached to an aromatic nucleus, the composition being further characterised by being storage stable but being curable by heat unblocking at 100 to 120 °C.

13. A composition according to claim 12 comprising a blocked polyisocyanate of formula (I) as defined in  
 25 any one of claims 1 to 10.

14. A composition according to claim 12 or claim 13 wherein the active hydrogen-containing compound is an amine or an alcohol.  
 30 15. A composition according to claim 14 wherein the active hydrogen-containing compound is 1,4-butanediol.

16. A composition according to any one of claims 12 to 15 further comprising a catalyst.  
 35 17. A composition according to claim 16 wherein the catalyst is dibutyl tin dilaurate or tri-ethylene diamine.

18. A composition according to any one of claims 12 to 17 wherein the active hydrogen-containing compound is a pigment carrier containing active hydrogen groups, the composition further comprising a pigment.  
 40 19. A composition according to any one of claims 12 to 18 having 0.5 to 2 blocked isocyanate groups per active hydrogen-containing group.

20. A process for coating a substrate comprising applying a composition according to any one of claims 12 to 19 to the substrate then heating the coating to a temperature of from 100 to 120 °C.  
 45

21. A process for coating a substrate which comprises electro-depositing onto the substrate a paint composition according to claim 20 and then heating the deposited paint to cross-link the pigment carrier.  
 50 22. A blocked polyisocyanate according to any one of claims 1 to 5 wherein R is an aromatic residue of an isocyanate compound selected from

55  $\omega,\omega'$ -diisocyanato-1,3-dimethyl benzene,  
 $\omega,\omega'$ -diisocyanato-1,4-dimethyl benzene,  
 $\omega,\omega'$ -diisocyanato-diethyl benzene,  
 $\omega,\omega'$ -diisocyanato-dimethyl toluene,  
 $\omega,\omega'$ -diisocyanato-diethyl toluene,

1,3-bis-(2-isocyanato-prop-2-yl) benzene and  
1,4-bis-(2-isocyanato-prop-2-yl) benzene.

5 23. A blocked polyisocyanate according to claim 22 wherein R is the residue of 1,3- bis-(2-isocyanato-prop-2-yl) benzene.

24. A process according to claim 11 wherein the polyisocyanate of formula

10  $R(NCO)_m$

is selected from

$\omega,\omega'$ -diisocyanato-1,3-dimethyl benzene,

$\omega,\omega'$ -diisocyanato-1,4-dimethyl benzene,

$\omega,\omega'$ -diisocyanato-diethyl benzene,

15  $\omega,\omega'$ -diisocyanato-dimethyl toluene,

$\omega,\omega'$ -diisocyanato-diethyl toluene,

1,3-bis-(2-isocyanato-prop-2-yl) benzene and

1,4-bis-(2-isocyanato-prop-2-yl) benzene.

20 25. A process according to claim 24 wherein the polyisocyanate of formula  $R(NCO)_m$  is 1,3-bis-(2-isocyanato-prop-2-yl) benzene.

26. A coating composition according to any one of claims 12 to 19 wherein R is an aromatic residue selected from the residues of

25  $\omega,\omega'$ -diisocyanato-1,3-dimethyl benzene,

$\omega,\omega'$ -diisocyanato-1,4-dimethyl benzene,

$\omega,\omega'$ -diisocyanato-diethyl benzene,

$\omega,\omega'$ -diisocyanato-dimethyl toluene,

30  $\omega,\omega'$ -diisocyanato-diethyl toluene,

1,3-bis-(2-isocyanato-prop-2-yl) benzene and

1,4-bis-(2-isocyanato-prop-2-yl) benzene.

35 27. A coating composition according to claim 26 wherein R is the residue of 1,3-bis-(2-isocyanato-prop-2-yl) benzene.

28. A process for coating a substrate comprising applying a composition according to claim 26 or claim 27 to the substrate then heating the coating to a temperature of from 100 to 120 °C.

40 29. A process for coating a substrate which comprises electro-depositing onto the substrate a paint composition according to claim 28 and then heating the deposited paint to cross-link the pigment carrier.

#### Patentansprüche

45 1. Blockiertes Polyisocyanat der Formel (I):

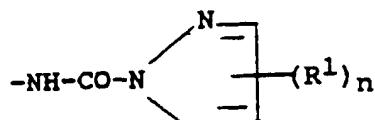
$R-Y_m$  (I)

50 worin m eine ganze Zahl größer als 1 bedeutet;

R einen m-valenten, cycloaliphatischen, heterocyclischen oder aromatischen Rest bedeutet;

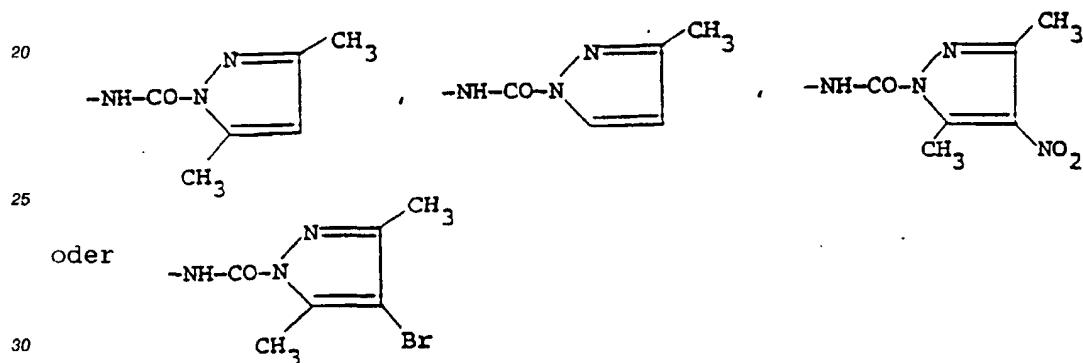
jedes Y, das gleich oder verschieden sein kann, für

55



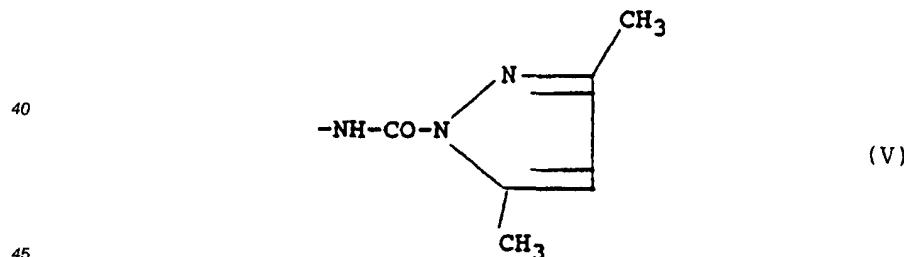
steht, worin n gleich 0, 1, 2 oder 3 ist;  
 wenn n gleich 1 ist, ist R<sup>1</sup> ausgewählt aus Alkyl, Alkenyl, Aralkyl, N-substituiertem Carbamyl, Phenyl, NO<sub>2</sub>, Halogen oder -CO-O-R<sup>2</sup>, wobei R<sup>2</sup> C<sub>1</sub>-C<sub>4</sub>-Alkyl bedeutet;  
 10 wenn n größer als 1 ist, können die Gruppen R<sup>1</sup> gleich oder verschieden sein und sind jeweils ausgewählt aus Alkyl, Alkenyl, Aralkyl, N-substituiertem Carbamyl, Phenyl, NO<sub>2</sub>, Halogen und -CO-OR<sup>2</sup>, wobei R<sup>2</sup> ein C<sub>1</sub>-C<sub>4</sub>-Alkyl bedeutet;  
 mit der Maßgabe, daß, wenn R für einen aromatischen Rest steht, die Gruppen Y nicht direkt an  
 15 den aromatischen Kern gebunden sind.

2. Blockiertes Polyisocyanat nach Anspruch 1, worin mindestens ein Y



bedeutet.

35 3. Blockiertes Polyisocyanat nach Anspruch 2, worin mindestens ein Y

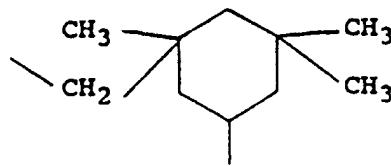


bedeutet.

50 4. Blockiertes Polyisocyanat nach einem der vorhergehenden Ansprüche, worin m 2 bis 6 ist.

5. Blockiertes Polyisocyanat nach einem der vorhergehenden Ansprüche, worin R eine Kohlenwasserstoffgruppe bedeutet, die wahlweise durch eine Alkoxygruppe substituiert ist.

55 6. Blockiertes Polyisocyanat nach Anspruch 1, worin R für einen divalenten, von Isophoron abgeleiteten Rest der Formel



10 steht.

7. Blockiertes Polyisocyanat nach einem der Ansprüche 1-6, worin R der Rest eines Polyisocyanat-Reaktionsproduktes aus einem Isocyanat und Wasser, einem niedermolekularen Polyol mit einem Molekulargewicht von weniger oder gleich 300 oder einem Polyol von einem mittleren Molekulargewicht ist, das ein Molekulargewicht von größer als 300 und weniger als 8000 aufweist.

15 8. Blockiertes Polyisocyanat nach Anspruch 7, worin R der Rest eines Polyisocyanat-Reaktionsproduktes aus einem Isocyanat und einem niedermolekularen Polyol ist, ausgewählt aus Ethylenglycol, Propylenglycol, 1,3-Butylen glycol, Neopentylglycol, 2,2,4-Trimethyl-1,3-pentandiol, Hexamethylenglycol, Cyclohexandimethanol, hydriertem Bisphenol A, Trimethylolpropan, Trimethylolethan, 1,2,6-Hexantriol, Glycerin, Sorbit und Pentaerythrit.

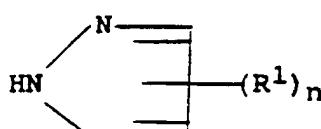
20 9. Blockiertes Polyisocyanat nach einem der Ansprüche 1-6, worin R der Rest eines Isocyanurats ist.

25 10. Blockiertes Polyisocyanat nach einem der vorhergehenden Ansprüche, das eine Biuretstruktur oder eine Allophanat-Gruppe aufweist.

11. Verfahren zum Herstellen eines blockierten Polyisocyanats nach einem der vorhergehenden Ansprüche, umfassend das Zusetzen eines Polyisocyanats der Formel

30  $R(NCO)_m$

zu einer Menge eines Pyrazols der Formel



40

worin R, m und n die in Anspruch 1 angegebene Bedeutung haben, so daß das Reaktionsprodukt keine freien Isocyanat-Gruppen enthält.

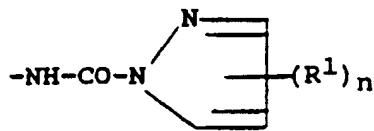
45 12. Beschichtungszusammensetzung, umfassend eine aktive wasserstoffhaltige Verbindung und ein blockiertes Isocyanat, dadurch gekennzeichnet, daß das blockierte Isocyanat eine Verbindung der Formel

$R-Y_m$

50 ist, worin m eine ganze Zahl größer als 1 bedeutet;

R einen m-valenten aliphatischen, cycloaliphatischen, heterocyclischen oder aromatischen Rest bedeutet;

55 jedes Y, das gleich oder verschieden sein kann,



bedeutet, worin n gleich 0, 1, 2 oder 3 ist;  
 wenn n gleich 1 ist, ist R<sup>1</sup> ausgewählt aus Alkyl, Alkenyl, Aralkyl, N-substituiertem Carbamyl,  
 10 Phenyl, NO<sub>2</sub>, Halogen oder -CO-O-R<sup>2</sup>, wobei R<sup>2</sup> C<sub>1</sub>-C<sub>4</sub>-Alkyl bedeutet;  
 wenn n größer als 1 ist, können die Gruppen R<sup>1</sup> gleich oder verschieden sein, und sind jeweils  
 15 ausgewählt aus Alkyl, Alkenyl, Aralkyl, N-substituiertem Carbamyl, Phenyl, NO<sub>2</sub>, Halogen und -CO-O-R<sup>2</sup>, wobei R<sup>2</sup> C<sub>1</sub>-C<sub>4</sub>-Alkyl bedeutet;  
 mit der Maßgabe, daß, wenn R für einen aromatischen Rest steht, die Gruppen Y nicht direkt an einen  
 20 aromatischen Kern gebunden sind, wobei die Zusammensetzung darüberhinaus dadurch gekennzeichnet  
 ist, daß sie lagerstabil, jedoch durch Wärmeentblocken bei 100-120 °C härtbar ist.

13. Zusammensetzung nach Anspruch 12, umfassend ein blockiertes Polyisocyanat der Formel (I) nach  
 einem der Ansprüche 1 bis 10.

20 14. Zusammensetzung nach Anspruch 12 oder Anspruch 13, in der die aktive wasserstoffhaltige Verbindung  
 ein Amin oder ein Alkohol ist.

15. Zusammensetzung nach Anspruch 14, in der die aktive wasserstoffhaltige Verbindung 1,4-Butandiol ist.

25 16. Zusammensetzung nach einem der Ansprüche 12 bis 15, die darüberhinaus einen Katalysator enthält.

17. Zusammensetzung nach Anspruch 16, in der der Katalysator Dibutyl-Zinndilaurat oder Triethylendiamin  
 ist.

30 18. Zusammensetzung nach einem der Ansprüche 12 bis 17, in der die aktive wasserstoffhaltige Verbindung  
 ein aktiver Wasserstoffgruppen enthaltender Pigmentträger ist, wobei die Zusammensetzung  
 darüberhinaus ein Pigment enthält.

35 19. Zusammensetzung nach einem der Ansprüche 12 bis 18, die 0,5-2 blockierte Isocyanat-Gruppen pro  
 aktiver wasserstoffhaltiger Gruppe aufweist.

20. Verfahren zum Beschichten eines Substrats, umfassend die Anwendung einer Zusammensetzung nach  
 einem der Ansprüche 12 bis 19 auf das Substrat und anschließendes Erhitzen der Beschichtung auf  
 40 eine Temperatur von 100-120 °C.

21. Verfahren zum Beschichten eines Substrats, umfassend elektrolytisches Abscheiden einer Anstrichzusammensetzung auf dem Substrat gemäß Anspruch 20 und anschließendes Erhitzen des abgeschiedenen Anstrichs zum Quervernetzen mit dem Pigmentträger.

45 22. Blockiertes Polyisocyanat nach einem der Ansprüche 1-5, worin R einen aromatischen Rest einer  
 Isocyanat-Verbindung ausgewählt aus

50     $\omega, \omega'$ -Diisocyanato-1,3-dimethyl-benzol,  
 $\omega, \omega'$ -Diisocyanato-1,4-dimethyl-benzol,  
 $\omega, \omega'$ -Diisocyanato-diethyl-benzol,  
 $\omega, \omega'$ -Diisocyanato-dimethyl-toluol,  
 $\omega, \omega'$ -Diisocyanato-diethyl-toluol,  
 55 1,3-Bis-(2-isocyanato-prop-2-yl)-benzol und  
 1,4-Bis-(2-isocyanato-prop-2-yl)-benzol  
 bedeutet.

23. Blockiertes Polyisocyanat nach Anspruch 22, worin R für den Rest 1,3-Bis-(2-isocyanato-prop-2-yl)-

benzol steht.

24. Verfahren nach Anspruch 11, worin das Polyisocyanat der Formel

5  $R(NCO)_m$

ausgewählt ist aus

$\omega, \omega'$ -Diisocyanato-1,3-dimethyl-benzol,  
 $\omega, \omega'$ -Diisocyanato-1,4-dimethyl-benzol,  
10  $\omega, \omega'$ -Diisocyanato-diethyl-benzol,  
 $\omega, \omega'$ -Diisocyanato-dimethyl-toluol,  
 $\omega, \omega'$ -Diisocyanato-diethyl-toluol,  
1,3-Bis-(2-isocyanato-prop-2-yl)-benzol und  
1,4-Bis-(2-isocyanato-prop-2-yl)-benzol.

15 25. Verfahren nach Anspruch 24, worin das Polyisocyanat der Formel  $R(NCO)_m$  1,3-Bis-(2-isocyanato-prop-2-yl)-benzol ist.

20 26. Beschichtungszusammensetzung nach einem der Ansprüche 12-19, worin R ein aromatischer Rest,  
ausgewählt aus den Resten

$\omega, \omega'$ -Diisocyanato-1,3-dimethyl-benzol,  
 $\omega, \omega'$ -Diisocyanato-1,4-dimethyl-benzol,  
 $\omega, \omega'$ -Diisocyanato-diethyl-benzol,  
25  $\omega, \omega'$ -Diisocyanato-dimethyl-toluol,  
 $\omega, \omega'$ -Diisocyanato-diethyl-toluol,  
1,3-Bis-(2-isocyanato-prop-2-yl)-benzol und  
1,4-Bis-(2-isocyanato-prop-2-yl)-benzol

30 ist.

27. Beschichtungszusammensetzung nach Anspruch 26, worin R für den Rest 1,3-Bis-(2-isocyanato-prop-2-yl)-benzol steht.

35 28. Verfahren zum Beschichten eines Substrats, umfassend die Anwendung einer Zusammensetzung nach  
Anspruch 26 oder Anspruch 27 auf das Substrat und anschließendes Erhitzen der Beschichtung auf  
eine Temperatur von 100 bis 120 °C.

40 29. Verfahren zum Beschichten eines Substrats, umfassend das elektrolytische Abscheiden einer Anstrich-  
zusammensetzung nach Anspruch 28 auf das Substrat und anschließendes Erhitzen des abgeschiede-  
nen Anstrichs zum Quervernetzen mit dem Pigmentträger.

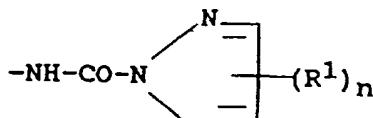
#### Revendications

45 1. Polyisocyanate bloqué de formule (I) :

$R-Y_m$  (I)

dans laquelle m est un entier supérieur à 1 ;

50 R est un reste m-valent, cycloaliphatique, hétérocyclique ou aromatique ;  
chacun des Y, pouvant être semblables ou différents, est



où n est 0, 1, 2 ou 3 ;

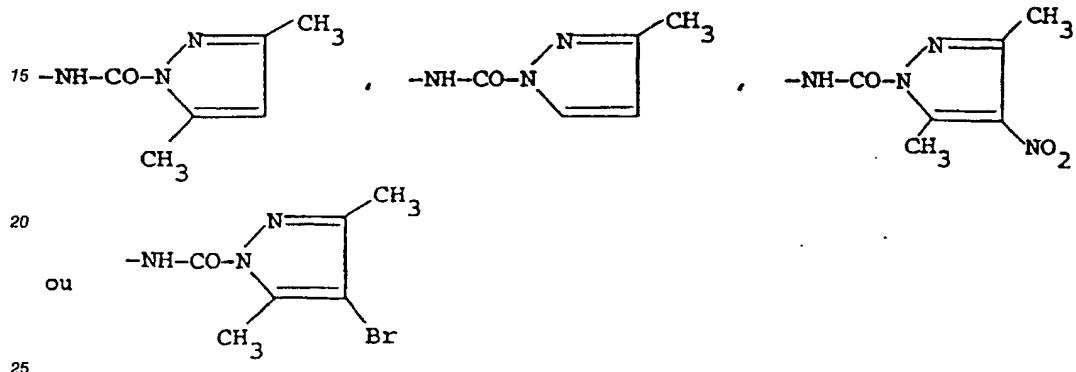
lorsque n est 1,

R<sup>1</sup> est choisi parmi alkyle, alcényle, aralkyle, carbamyle N-substitué, phényle, NO<sub>2</sub>, halogène ou -CO-O-R<sup>2</sup>, où R<sup>2</sup> est un alkyle en C<sub>1</sub>-C<sub>4</sub> ;

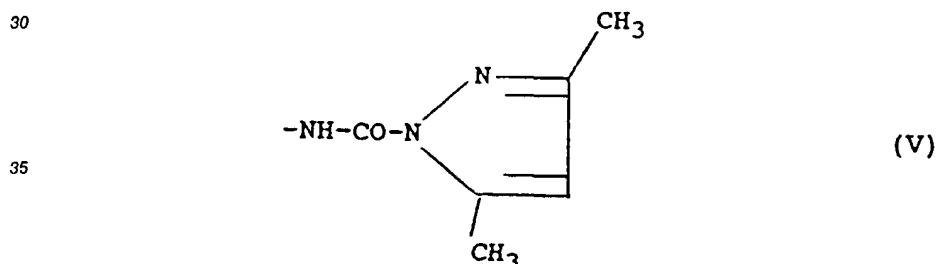
lorsque n est supérieur à 1, les groupes R<sup>1</sup> peuvent être semblables ou différents et sont choisis chacun parmi alkyle, alcényle, aralkyle, carbamyle N-substitué, phényle, NO<sub>2</sub>, halogène et -CO-O-R<sup>2</sup>, où R<sup>2</sup> est un alkyle en C<sub>1</sub>-C<sub>4</sub> ;

sous réserve que, lorsque R est un reste aromatique, les groupes Y ne soient pas fixés directement à un noyau aromatique.

10 2. Polyisocyanate bloqué selon la revendication 1, dans lequel au moins un Y est



3. Polyisocyanate bloqué selon la revendication 2, dans lequel au moins un Y est

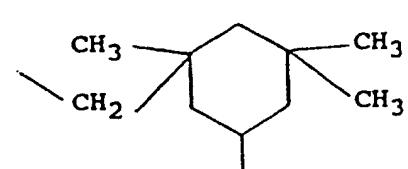


40 4. Polyisocyanate bloqué selon l'une quelconque des revendications précédentes, dans lequel m a une valeur de 2 à 6.

45 5. Polyisocyanate bloqué selon l'une quelconque des revendications précédentes, dans lequel R est un groupe hydrocarboné facultativement substitué par un groupe alcoxy.

6. Polyisocyanate bloqué selon la revendication 1, dans lequel R est un radical divalent dérivé de l'isophorone de formule :

50

55 

7. Polyisocyanate bloqué selon l'une quelconque des revendications 1 à 6, dans lequel R est le reste d'un produit de type polyisocyanate résultant de la réaction d'un isocyanate et de l'eau, d'un polyol de faible poids moléculaire ayant un poids moléculaire inférieur ou égal à 300 ou d'un polyol de poids moléculaire moyen ayant un poids moléculaire supérieur à 300 et inférieur à 8 000.

5 8. Polyisocyanate bloqué selon la revendication 7, dans lequel R est le reste d'un produit de type polyisocyanate résultant de la réaction d'un isocyanate et d'un polyol de faible poids moléculaire choisi parmi l'éthylèneglycol, le propylèneglycol, le 1,3-butylèneglycol, le néopentylglycol, le 2,2,4-triméthyl-1,3-pantanediol, l'hexaméthylèneglycol, le cyclohexanediméthanol, le bisphénol-A hydrogéné, le triméthylolpropane, le triméthyloléthane, le 1,2,6-hexanetriol, la glycérine, le sorbitol et le pentaérythritol.

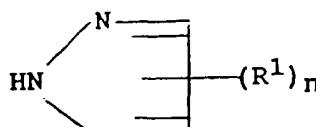
10 9. Polyisocyanate bloqué selon l'une quelconque des revendications 1 à 6, dans lequel R est le reste d'un isocyanurate.

15 10. Polyisocyanate bloqué selon l'une quelconque des revendications précédentes, qui a une structure de biuret ou un groupe allophanate.

11. Procédé pour préparer un polyisocyanate bloqué selon l'une quelconque des revendications précédentes, qui comprend le mélange d'un polyisocyanate de formule

20  $R(NCO)_m$

avec une quantité d'un pyrazole de formule



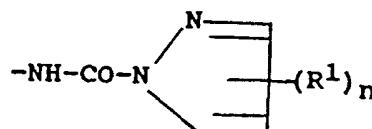
30

dans laquelle R, m et n sont comme définis dans la revendication 1, telle que le produit de la réaction ne contienne pas de groupes isocyanates libres.

35 12. Composition de revêtement qui comprend un composé contenant de l'hydrogène actif et un polyisocyanate bloqué, caractérisée en ce que le polyisocyanate bloqué est un composé de formule

$R-Y_m$

40 dans laquelle m est un entier supérieur à 1 ;  
 R est un reste m-valent aliphatic, cycloaliphatic, hétérocyclique ou aromatique ;  
 chacun des Y, pouvant être semblables ou différents, est



50

où n est 0, 1, 2 ou 3 ;

lorsque n est 1,

R¹ est choisi parmi alkyle, alcényle, aralkyle, carbamyle N-substitué,

phényle, NO₂, halogène ou -CO-O-R² où R² est un alkyle en C₁-C₄ ;

lorsque n est supérieur à 1,

les groupes R¹ peuvent être semblables ou différents et sont choisis chacun parmi alkyle, alcényle, aralkyle, carbamyle N-substitué,

phényle, NO₂, halogène et -CO-O-R², où R² est un alkyle en C₁-C₄

;

sous réserve que, lorsque R est un reste aromatique, les groupes Y ne soient pas fixés directement à

un noyau aromatique, la composition étant de plus caractérisée en ce qu'elle est stable au stockage, mais peut être durcie par déblocage à chaud entre 100 et 120 °C.

13. Composition selon la revendication 12, comprenant un polyisocyanate bloqué de formule (I) comme défini dans l'une quelconque des revendications 1 à 10.

14. Composition selon la revendication 12 ou la revendication 13, dans laquelle le composé contenant un hydrogène actif est une amine ou un alcool.

15. Composition selon la revendication 14, dans laquelle le composé contenant un hydrogène actif est le 1,4-butanediol.

16. Composition selon l'une quelconque des revendications 12 à 15, comprenant de plus un catalyseur.

17. Composition selon la revendication 16, dans laquelle le catalyseur est le dilaurate de dibutylétain ou la triéthylènediamine.

18. Composition selon l'une quelconque des revendications 12 à 17, dans laquelle le composé contenant de l'hydrogène actif est un porteur de pigment contenant des groupes à hydrogène actif, la composition comprenant de plus un pigment.

19. Composition selon l'une quelconque des revendications 12 à 18, ayant 0,5 à 2 groupes isocyanates bloqués par groupe contenant de l'hydrogène actif.

20. Procédé pour revêtir un substrat, comprenant l'application d'une composition selon l'une quelconque des revendications 12 à 19 au substrat, puis le chauffage du revêtement à une température de 100 à 120 °C.

21. Procédé pour revêtir un substrat, comprenant l'électro-déposition sur le substrat d'une composition de peinture selon la revendication 20 puis le chauffage de la peinture déposée pour réticuler le porteur de pigment.

22. Polyisocyanate bloqué selon l'une quelconque des revendications 1 à 5, dans lequel R est un reste aromatique d'un composé isocyanate choisi parmi l' $\omega,\omega'$ -diisocyanato-1,3-diméthylbenzène, l' $\omega,\omega'$ -diisocyanato-1,4-diméthylbenzène, l' $\omega,\omega'$ -diisocyanatodiéthylbenzène, l' $\omega,\omega'$ -diisocyanatodiméthyltoluène, l' $\omega,\omega'$ -diisocyanatodiéthyltoluène, le 1,3-bis(2-isocyanato-prop-2-yl)benzène et le 1,4-bis(2-isocyanato-prop-2-yl)benzène.

23. Polyisocyanate bloqué selon la revendication 22, dans lequel R est le reste du 1,3-bis(2-isocyanato-prop-2-yl)benzène.

24. Procédé selon la revendication 11, dans lequel le polyisocyanate de formule R(NCO)<sub>m</sub> est choisi parmi l' $\omega,\omega'$ -diisocyanato-1,3-diméthylbenzène, l' $\omega,\omega'$ -diisocyanato-1,4-diméthylbenzène, l' $\omega,\omega'$ -diisocyanatodiéthylbenzène, l' $\omega,\omega'$ -diisocyanatodiméthyltoluène, l' $\omega,\omega'$ -diisocyanatodiéthyltoluène, le 1,3-bis(2-isocyanato-prop-2-yl)benzène et le 1,4-bis(2-isocyanato-prop-2-yl)benzène.

25. Procédé selon la revendication 24, dans lequel le polyisocyanate de formule  $R(NCO)_m$  est le 1,3-bis(2-isocyanato-prop-2-yl) benzène.

26. Composition de revêtement selon l'une quelconque des revendications 12 à 19, dans laquelle R est un reste aromatique choisi parmi les restes de  
5 l' $\omega,\omega'$ -diisocyanato-1,3-diméthylbenzène,  
l' $\omega,\omega'$ -diisocyanato-1,4-diméthylbenzène,  
l' $\omega,\omega'$ -diisocyanatodiéthylbenzène,  
l' $\omega,\omega'$ -diisocyanatodiméthyltoluène,  
10 l' $\omega,\omega'$ -diisocyanatodiéthyltoluène,  
le 1,3-bis(2-isocyanato-prop-2-yl)benzène et  
le 1,4-bis(2-isocyanato-prop-2-yl)benzène.

27. Composition de revêtement selon la revendication 26, dans laquelle R est le reste du 1,3-bis(2-isocyanato-prop-2-yl)benzène.

28. Procédé pour revêtir un substrat comprenant l'application d'une composition selon la revendication 26 ou la revendication 27 au substrat, puis le chauffage du revêtement à une température de 100 à 120 °C.

20 29. Procédé pour revêtir un substrat qui comprend l'électro-déposition sur le substrat d'une composition de peinture selon la revendication 28, puis le chauffage de la peinture déposée pour réticuler le porteur de pigment.

25

30

35

40

45

50

55